State Form 4336

DEPARTMENT OF ENVIRONMENTAL MANAGEMENT
INDIANAPOLIS

OFFICE MEMORANDUM ***Not for Public Release**

Date: 12-04-13

To: Carmen Anderson, PM,

Thru: Barry Steward, Chief;
Jeff Moody,
Engineering & GIS Services

From: Susan Horein
Environmental Engineer
Engineering & GIS Services

Subject**:** **Soil Gas Methane/ RWP**
Michigan Plaza
Indianapolis, Marion County
VRP # 6061202

Summary:
Mundell and Associates (Mundell) has been attempting to create an in-situ anaerobic chlorinated bioremediation zone at the Michigan Plaza site through a series of CAP 18 injections dating to 2007. The most recent injections occurred in July, 2013 as outlined in the "Second Revised Work Plan for the Third Round of CAP-18 ME Injections (Feb. 20, 2013). In addition, Mundell has corresponded with IDEM through a series of email proposals to deal with subsequent high levels of methane generated from the injections.

In the 3rd Quarter 2013 Quarterly Monitoring Progress Report, the methane concentration at groundwater monitoring well MMW-12S (screened 14-24 ft bgs; depth to water listed as 15.7 ft bgs) was indicated as 29,100 ppmv which is approximately 3% methane. The lower explosive limit (LEL) for methane is 5%. Several on site structures have radon type mitigation systems for vapor intrusion (VI) issues. Methane was detected at nominal concentrations in the effluent from these mitigation systems.

Mundell subsequently installed 12 nested soil gas monitoring wells (MGWs) to better assess methane at the site. The shallow soil gas wells are screened from 5-6 ft bgs while the deep soil gas wells are screened from 11-12 ft bgs. October 23rd sampling indicated 1.7% methane at MGW8-D while MGW8-S had only 0.002% methane. The samples were taken with a calibrated gas meter and Mundell indicated additional biweekly meter readings would occur in addition to collecting samples for analysis as part of the 4th quarter sampling.

A November 14th email indicated fittings allowing pressure readings and air samples would be installed but did not indicate if it was soil gas or monitoring wells or both. Mundell completed an additional round of sampling the week of November 22. Readings taken with

an Eagle RKI Gas meter indicated MGW-08D had concentrations in excess of 5% methane while MGW-06D has concentrations >3% methane. Mundell corrorborated with gas company officials who showed readings of 3% at MGW-08D and 1.2% at MGW-06D. Mundell indicated shallow gas wells and indoor air did not show concentrations of concern but did not report concentrations in the November 22nd email.

Mundell agreed to mobilize an SVE system to assess 'the ability to control the vapors". The mobile SVE was connected to groundwater MW-8S (screened 14-24 ft - DTW 17.5 ft bgs) as it had three foot of screen above the water table. The system operated for about four hours at 160 cfm. Methane in MGW-8D (adjacent) dropped from >5% methane to less than 0.01% methane. Readings the next day indicated 0.15% methane while two days later readings indicated 0.21% methane. Subsequent mobile SVE testing (November 27, 2013) at MMW-P-11S and MMW-12S was completed to assess the ability to capture methane in the area of MGW-6D and MGW-11D which had also shown elevated methane readings.

General Comments:

1. Substantial soil gas methane exists on site. Dedicated gas monitoring wells screened from 11-12 ft bgs had concentrations greater than 25% of the LEL for methane and have exhibited concentrations equal to the LEL (MGW-08D) in at least one instance. IDEM's landfill methane monitoring program indicates methane soil gas should be mitigated if it is in excess of 25% methane while at least two states (Minnesota (http://www.pca.state.mn.us/index.php/view-document.html?gid=13963 and Wyoming http://deq.state.wy.us/shwd/stp/STPDownloads/Guidance/Guidance_16.pdf) guidance for anaerobic ethanol fuel sites indicate addressing methane at greater than 10% soil gas methane is appropriate. Substantial attenuation appears to be occurring before methane reaches receptors, but the concentrations warrant mitigation.

2. The preferential pathway analysis for methane has not been a comprehensive stepwise delineation but has instead been based on currently available sub slab ports and gas monitoring wells. Subslab concentrations had nominal levels of methane. Utilities and other preferential pathways are not delineated but given the heterogeneous nature of the site due to the fact that it is highly developed with multiple structures and utility corridors in extremely close proximity, ruling out all possible preferential methane migration pathways would be difficult. Several groundwater wells beneath on site structures had concentrations in the tens of thousand of micrograms per liter. For example MMW-P-10D screened (28-38 ft bgs), which appears to be beneath the Village Pantry parking lot, had methane concentrations of 29,800ug/L while MMW-P-10S (screened 18-28 ft bgs) had concentrations of 11,800ug/L. Given the substantial methane concentrations being continually generated and the difficulty of ruling out all preferential pathways, mitigation as Mundell has proposed is appropriate. Mundell indicates pressure readings have been collected in conjunction with monitoring events. These should be submitted along with a conceptual site analysis to determine the coverage needed for the SVE system. A table of methane concentrations to date would be extremely useful.

3. Mundell indicates in multiple correspondences that the CAP 18 is likely not the

methane source based on groundwater concentrations.

a. Engineering Services believes that groundwater concentrations in excess of 1-2,000 ug/L are capable of generating methane at the LEL if attenuation does not occur (see Appendix B taken from OLQ Draft document, “Addressing Methane at Anaerobic Dechlorination Sites). Site groundwater concentrations are well in excess of this. However, Henry’s law is not particularly suited at predicting methane concentrations as it mainly applies to dilute solutions and does not account for any attenuation before a source is reached.
b. The solubility of methane is 22-30,000 ug/L based on pressure and temperature. Groundwater concentrations during 9/24/2013 sampling at MMW-8S were 25,000 ug/l. MMW-1S had 24,700 ug/l while MMW-P-03 had 21,000 ug/L with multiple other instances of methane concentrations approaching solubility. If solubility is exceeded, methane will off gas from the groundwater.
c. Mundell has not made an adequate alternate source demonstration to show that sewer gas is the source. Several anomalies would need to be explained for this theory to be valid:
    i. MGW-8D is below the sewer invert but has the highest concentration of methane on site. Methane is less dense than air and would rise in the absence of any temperature differential.
    ii. Sewer gas has a characteristic composition which would be expected to be different than remediation generated methane. Hydrogen sulfide was only indicated at the sewer manhole but not in any of the gas well samples. A characterization of the sewer gas would need to be compared to a gas well sample to support this theory.

Recommendations:

1. The sustained generation of methane should be addressed. The proposed collection system is advised and should be implemented as soon as possible. Start up vacuum monitoring should be done to ensure design radii are achieved and that short circuiting due to utility corridors is not occurring.
2. An adequate alternate source demonstration has not been done to show that CAP-18 is not the source of the methane.

Appendix B – Screening Level Explanation

Not enough data exists for a data-driven analysis of a ground water methane concentration screening level indicative of hazardous conditions. Henry's Law predicts 1-2 mg/L in the ground water could theoretically produce 5% methane (see below). However, using only Henry's Law does not account for any oxygen consumption of methane. USGS (2006) indicated 10 mg/L as a screening level but did not support the concentration with a stringent numerical analysis. Nevertheless, 10 mg/L is about half the solubility and seems like a reasonable indication that the site's microbial population is generating substantial ground water methane and soil gas methane should be investigated if receptors are present.

Using Henry's Law to Predict Ground Water Concentrations Leading to 5% Methane

Dimensionless H_{CH4} = 28 (mass based)

P_{atm} = 101.325 kPa = 1.013 bars

Methane LEL = 5% which means $\frac{P_{\text{methane}}}{P_{\text{atmosphere}}} = 0.05$

$P_{methane}$ = (0.05)(P_{atm}) = (0.05)(101.325 kPa) = 5.06 kPa = partial pressure of methane that equates to 5% methane.

Compute the gaseous concentration that equates to 5.06 kPa.

Use $PV \equiv nRT$:

$$\frac{n}{V} \equiv \frac{P}{RT}$$

$$\frac{n}{V} \equiv \frac{P}{RT} = \frac{5.06 kPa}{(8.3144 L*kPa/mol*K)(298 K)} = 0.002 \text{mol/L gas}$$

Convert 0.002 mol/L to gm/L,
Methane = 16 gm/mol such that:
(0.002 moles/l)(16 gm/mol) = 0.032 gm/L of methane.

Estimate the ground water methane concentration leading to 0.032 gm/L of gas phase methane using dimensionless Henry's Law constant of 28.

$$H \equiv \frac{C_{gas}}{C_{water}} = 28$$

$C_{water} \equiv \frac{C_{gas}}{H}$ = 0.032/28 = 0.001gm/L ~ 1mg/L (Assumes STP).

In theory, dissolved methane between 1 and 2 mg/L (depending on ground water temperature) exceeds the LEL at the water surface based on Henry's Law.

Or use an actual Henry's Law constant instead of the dimensionless 28.

P_{atm} = 101.325 kPa = 1.013 bars
5% methane = 0.0506 bars.

$H_{CH4=} \frac{0.0014 mol}{kg * bar}$

(**Lide and Frederikse; 1995; CRC Handbook of Chemistry and Physics, 76th Edition**; D. R. Lide and H. P. R. Frederikse, ed(s); CRC Press, Inc.; Boca Raton, FL, 1995.)

(Note: Concentration based Henry's Law constant is the inverse of the dimensionless form.)

$H \equiv \frac{C_{water}}{C_{gas}}$

$mol/kg \equiv . \frac{0.0014 mol}{Kg \text{ bar}} \frac{0.0506 bar}{} = 0.00007 mol/Kg$ (Assumes STP and Ideal solution)

1Kg water = 1L
1 mole methane = 16 gm

$\frac{0.00007 mol}{Kg} * \frac{1 Kg}{L} * \frac{16 \text{gm } CH_4}{\text{mole } CH_4} * \frac{1000 mg}{gm} = 1.13 \frac{mg}{L} \ CH_4$